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EXPERIENCES IN STUDYING ORGANIC TASTE AND ODOR SUBSTANCES IN WATER, USING CARBON FILTER SAMPLING METHODS

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Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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The Problem of Organic Chemicals in Water

Rapid industrial growth and the phenomenal increase in the manufacture of synthetically produced chemicals unheard of a few years ago has produced new problems of stream pollution stemming from the discharge of organic wastes into surface waters. Table 1 is indicative of recent production of several of these materials and shows estimates of future production[1,2]. A doubling of chemical sales between 1940 and 1950 and further anticipated industrial expansion make it imperative that the effects of organic waste products as an environmental health factor be determined.

Organic materials may also reach surface waters through the discharge of domestic sewage and natural run-off. The significant contribution of organic materials due to life and death processes of aquatic plants and animals is a little understood facet of the total problem. These effects due to nature may be greatly influenced by man's activity. Increased supplies of phosphorus and nitrogen from sewage or other sources may stimulate extensive growth of algae or other aquatic life.

The complexities of disposal of wastes from organic chemicals manufacture are discussed by Hess and Carney[5]. The residues of large diversified manufacturing plants may contain thousands of complex compounds including by-products, process aids, unreacted raw materials, and

the product itself. The volume of these materials may be as large as that of the main product. Practical and economical disposal of such materials is difficult and complete elimination may be impossible.

The effect of the diverse mixtures of organic materials on water and on the consumer of drinking water taken from sources containing such pollution deserves critical evaluation. Important known effects of these materials are the production of taste and odor in water and interferences with water treatment. Relatively unexplored are the possible physiological effects of such materials. Wedgewood[3,4] has detected polynuclear hydrocarbons in waste effluents and sewage effluents. Such materials are known to possess carcinogenic characteristics. An extensive review of the literature on the toxicity of materials known to be discharged to water and actual studies of selected materials have been undertaken[6].

Carbon Filter Studies

There are with few exceptions no standard selective and specific methods for the analysis of the multitude of organic chemicals occurring in water. Many of the materials are not sufficiently reactive to offer a sensitive means for identification. Furthermore, ordinary analytical techniques are usually inapplicable due to the extremely low concentrations present. Some means of concentrating the materials for analysis is necessary. The carbon filter has been used for this purpose. Briefly, organic materials are adsorbed onto active carbon by passing the water or waste through small filters. The carbon is dried and eluted with chloroform. The solvent is removed and the residue is subjected to further analysis. Details of the use of this filter and certain applications to taste and odor studies have been described[7,8]. It is the purpose of this paper to discuss improvements

in the method subsequent to previous publications, the usefulness and limitation of the technique and to show by example the types of analyses undertaken.

Sampling

The present sampling method is to pass 1,000 to 10,000 gallons of water or a lesser amount of liquid waste through one or more filters. If suspended matter is a factor the sample is prefiltered through 4-10 mesh Cliffchar carbon*. This filter is followed by one containing Nuchar C-190** unground carbon. The flow characteristics are often improved by placing the 4-10 mesh carbon in each end of the second filter. Backwashing is avoided if possible. Sand may be used as a prefilter but substantial losses of material may occur. This is particularly true of oily materials. A laboratory carbon filter installation for concentrating materials from tap water is shown in Figure 1.

Recovery of Materials

The concentrations of organic materials in various waters as indicated by the carbon filter technique range from a few parts per billion (p.p.b.) to more than 3,000 p.p.b., (3.0 parts per million). Table 2 shows the quantities recovered from various waters. Raw waters do not necessarily have greater concentrations of organic materials than do finished waters at the same location unless active carbon is applied or other specific methods for removal of the organic materials are used.

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*Product of Cliffs Dow Chemical Company, Marquette, Michigan

**Product of West Virginia Pulp and Paper Company
Industrial Chemical Sales Div.,
230 Park Avenue, New York, New York

Recovery of materials by the carbon filter is not quantitative. Adsorption and desorption on carbon depend on numerous factors, some of which are little understood. Uniform operation of two filters and similar treatment of samples in the laboratory yields results reproducible within the precision of measuring water flows. Table 3 indicates the recoveries obtained from a series of duplicate samples of Cincinnati water.

When it was necessary to sample large volumes of water in order to obtain sufficient extract for investigation, relatively low volumes of water were passed through each of several filters, arranged in a parallel bank. This arrangement was more rapid and efficient than the use of a single filter for large volumes of water.

To study the relationship of the quantities of materials adsorbed and desorbed by this technique known quantities of phenol were adsorbed from solution onto carbon and eluted in a standard manner. Table 4 shows the recoveries obtained by this method in one series of tests. In each instance the weight of phenol in column 1 was dissolved in 200 ml. of distilled water. Three grams of Nuchar C-190 were added to the solution. The mixture was agitated for 30 minutes and allowed to stand overnight after which the carbon was filtered off, dried and extracted with chloroform. Recovery of phenol ranged from 61 to 77 percent of the quantity adsorbed. Prolonged extraction had little effect in increasing the yield.

Duplicate samples of oily wastes have been tested by the carbon filter method and by liquid-liquid extraction. Filter recoveries were approximately 90 percent of those obtained by liquid extraction. The extraction method is considered to effect almost complete recovery of such materials.

Due to the incomplete recoveries of organic materials from the carbon it is well to consider whether the materials recovered are representative of the materials adsorbed. In addition the possibility of chemical change occurring on the highly active surface of the carbon should not be overlooked. Phenol, a material that may be readily oxidized in a stream, does not appear to undergo chemical change by being adsorbed on carbon followed by elution with chloroform. Present evidence for this statement is based on infrared and ultra violet spectra of the recovered product. DDT, a stable aromatic compound, survives the carbon technique unchanged. Refinery waste materials recovered by wet extraction methods correspond closely in composition with similar samples collected by the carbon filter method. Undoubtedly certain highly reactive materials may undergo changes on carbon. However, such materials in water will usually have already been stabilized by normal oxidation or other reactions.

The carbon filter technique can be applied only to those materials which are adsorbed from water by active carbon and which can be subsequently extracted from the carbon. It is further limited by the present extraction and recovery processes to materials that boil higher than chloroform (b.p. 61° C.). Such compounds as low boiling mercaptans, aldehydes and lower alcohols would be missed. These volatile materials may cause trouble if they travel rapidly from the pollution source to the drinking water. Under conditions of cold weather or ice coverage the volatiles may persist for long periods. Other techniques may be applied to the detection of such substances. A method for determining volatile contaminants in water using the mass spectrometer has been published by Melpolder, Warfield and Headington[9].

The materials recovered by the carbon filter are usually highly odorous. Sufficient quantities of chemicals can be recovered to permit studies not previously possible. To supplement and improve where possible the total study of organics in water, liquid-liquid extraction methods are also being investigated.

Specific Applications of the Carbon Filter

Refinery Waste Studies

Gravity oil separator effluents and waters near refinery waste discharges have been tested rather extensively by means of the carbon filter technique. The purpose of these tests was to attempt to determine the principal taste and odor constituents of this waste. In addition the application of the method offered a possible approach for the identification of petroleum refinery wastes in water. Details of these studies have been published or presented[10,11]. The following summary illustrates the techniques used and indicates the possible applications.

The extracts as recovered from the carbon are usually gross mixtures and little of the actual chemical composition is revealed unless separation of the material is undertaken. Initial separation is accomplished by application of extractions under various conditions, taking advantage of differential solubilities of organic groups. The principal groups separated by this method are acids, bases, neutrals and phenols. The relative proportions of these groups in several refinery wastes are shown in Table 5.

The most important group on the basis of quantity and odor intensity was the neutral materials. These substances were largely aliphatic and aromatic hydrocarbons. A fractional distillation of the neutral materials was performed, which revealed that odorous materials in these samples covered a wide range of boiling points.

Sulfur compounds are frequently associated with odors from petroleum processes. Treatment of the neutral materials to remove mercaptans, known to be highly odorous, reduced the sulfur content slightly, but had little affect on the total odor intensity.

By means of chromatographic techniques the neutral materials were separated into aliphatic, aromatic and "oxy" compounds. This step in the separation and purification process of these samples is the key to possible identification of these materials in water. The infrared spectra of such materials are characteristic and similarity of the spectra of materials isolated from water by comparable techniques is strong evidence for the presence of oil wastes in water. Outwardly such waters may give no appearance of oil. Figure 2 shows the infrared spectra of the aliphatic portion of waste material from five different refineries, and the infrared spectrum of the aliphatic portion of an extract recovered from a raw water source for a city near one refinery area. The marked similarity of these curves is considered to be evidence for the presence of petroleum wastes in this water supply.

Threshold odor concentrations using the water dilution technique were determined on the various groups and fractions of the oil waste. Table 6 shows the threshold results on the refinery waste components. In general a few parts per billion of such materials can be detected by laboratory odor tests. Substances of this type require tremendous dilution to become unobjectionable in water.

Isolation of DDT

A unique incident serves to demonstrate further the application of the carbon filter to water studies. In this instance the infrared spectra of extracts from both raw and finished water indicated DDT or structurally

related compounds. This finding was incidental to the search for taste and odor bearing materials. To confirm the presence of the insecticide, the extract was separated and purified. The DDT concentrated in the aromatic portion obtained by chromatographing the neutral group. Figure 3 shows the infrared spectra of the raw water extract, the aromatic portion, and a commercial sample of DDT. The absorption bands at 9.18 and 9.85 microns are the most significant characteristics of the material. The presence of DDT was further confirmed by colorimetric tests and elemental analysis on a purified sample. It was estimated that the water sampled contained 1 to 5 p.p.b. of DDT. This material was found over a period of several months, after which it no longer could be detected.

A Musty Component in Water

Another material as yet unidentified has been recovered from several waters including the Ohio River, the Mississippi River, the Scioto River, and the Great Lakes. This substance is obtained by collecting and purifying the steam distillate of the neutral group. The odor of this chemical is extremely musty, particularly when dilute. The same odor was conspicuously present in the waters from which these samples were obtained. Present evidence indicates that the musty material is an ester. It appears to be of natural origin and is not believed to be related to industrial wastes. It has recently been suggested by Silvey[12,13,14] that musty odors and others are due to actinomycetes found growing within algae cells.

Detergent Episode at Wheeling, West Virginia

Synthetic detergents may create problems at water purification plants. Culp and Stoltenberg[15] have reviewed an incident in Kansas where water purification was seriously affected by detergents. The Wheeling, West Virginia

water plant experienced excessive foaming and detergent pollution following the flush out of streams after a long period of dry weather. Todd[16] has described this episode, which was marked by foam three feet high on the water basins. He collected a portion of this material and permitted it to liquefy. Samples of this liquid proved to contain in excess of 1,000 p.p.m. of anionic type active detergent material. The water at Wheeling during this period contained from 1 to 12 p.p.m. of detergent as measured by the methylene blue method, a general method for anionic detergents.

Further information concerning the principal materials in the foam was desired. A sample of the liquefied foam was shaken with active carbon and then filtered. The filtrate did not foam. The carbon was extracted with chloroform and then with ethyl alcohol. The alcoholic extract was evaporated to a film and the infrared spectrum obtained, which was compared with the spectrum of a pure alkyl aryl sulfonate. The latter compound represents the most widely used class of detergent materials. Figure 4 is the infrared spectra of the two materials. The striking similarity of the spectra leaves little doubt that the foam material was principally alkyl aryl sulfonate.

Water from Wheeling during the period of detergent contamination was passed through carbon filters. Initial attempts to recover the materials from the carbon were not successful. The application of active carbon to problems of pollution by detergents is being investigated further.

SUMMARY

The carbon filter provides a means for recovering from water and waste small quantities of organic substances for which no direct methods of analysis are available. The techniques of using the filter and recovering the materials are discussed. Specific applications of the filter

to problems of taste and odor in refinery effluents, an approach to identification of refinery wastes in water, recovery of an insecticide, recovery of a musty component and detergents in water are pointed out.

Acknowledgement

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Table 1

Recent and Estimated Production of Certain Synthetic Organic Chemicals

Year	Detergents	Plastics	Organic Agricultural Chemicals		
			DDT	Benzene Hexachloride	Toxaphene, Chlordan Aldrin and Dieldrin
	Millions of Pounds				
1947	-	-	50	8	-
1950	1660	2280	-	75	40
1952	-	-	105	160	115
1955	2000	3500	125	170	-
1960	2500	4800	155	200	-
1975	4000	9000	200	225	-

TABLE 2

RECOVERY OF ORGANIC MATERIALS FROM VARIOUS WATERS BY THE CARBON FILTER METHOD

Location	No. of Samples	Water Source	Sample Source	Pollutional Characteristics	Recovery of Organic Materials Parts Per Billion		
					Max.	Min.	Av.
Cincinnati, Ohio	38	Ohio River	Finished Water	Sewage and Industrial Waste	630	79	220
Nitro, West Virginia	14	Kanawha River	Raw Water	Chemical Waste	3060	170	930
Columbus, Ohio	3	Scioto River	Raw Water	None	82	38	62
Piketon, Ohio	2	Scioto River	Raw Water	Sewage and Industrial Waste	606	587	597
Wyandotte, Michigan	4	Detroit River	Finished Water	Industrial Waste Sewage	366	38	203
Saginaw, Michigan	1	Lake Huron	Finished Water	None	—	—	25

TABLE 3

REPRODUCIBILITY OF CARBON FILTER SAMPLES*

SAMPLE NO.	GALLONS FILTERED	ORGANICS RECOVERED	
		GRAMS	P.P.B.
1	3180	1.84	152
1-A	3500	2.29	165
2	5810	2.89	125
2-A	6230	3.00	126
3	4378	2.32	133
3-A	4104	2.33	142
4	4100	2.49	160
4-A	6860	6.70	177
5	3900	3.47	234
5-A	4000	3.50	231
6	1600	3.1	515
6-A	1650	3.2	513

*ALL SAMPLES FROM CINCINNATI TAP WATER USING NUCHAR C-190 CARBON

TABLE 4

RECOVERY OF PHENOL FROM NUCHAR C-190 UNGROUND CARBON BY CHLOROFORM EXTRACTION

Phenol Applied	Phenol Adsorbed	Phenol Desorbed	Percentage Recovery of Adsorbed Phenol
Grams			
0.10	0.099	0.077	77.1
0.25	0.247	0.166	67.2
0.50	0.461	0.338	73.3
0.75	0.580	0.353	60.8
1.00	0.637	0.428	67.3
3.00	0.910	0.556	61.0

TABLE 5

GROUP SEPARATION OF CARBON FILTER EXTRACTS FROM OIL SEPARATOR EFFLUENTS [a]

Refinery	Sample No.	Neutral Group Percent	Phenolic Group Percent	Acidic Group Percent	Basic Group Percent	Loss Percent
A	A-1	84.5	3.7	0.15	0.44	11.2
	A-2	78.5	4.5	1.0	1.0	15.0
B	B-1	57.5	24.7	1.9	1.4	10.9
	B-2	85.0	1.3	0.5	4.4	9.1
	B-3	85.0	4.2	0.3	0.4	9.3
C	C-1	87.5	0.6	0.2	4.5	7.2
E	E-1	64.0	1.1	0.9	0.33	33.0[b]
	E-2	87.4	0.7	11.1	--	0.8

(a) Sample E-2 was obtained by liquid extraction. All others were obtained by carbon filter technique.

(b) Excessive loss unaccounted for.

TABLE 6

THRESHOLD ODOR CONCENTRATIONS OF OIL SEPARATOR EFFLUENT EXTRACTS

Threshold Odor Concentration[a] - Parts per Billion

Refinery	A			B			C			E					
Sample No.	A-2			B-3			C-1			E-1			E-2		
Sample Source	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
Total Extract	64	16	25	128	16	37	64	16	32	64	16	28	256	16	52
GROUPS															
Acidic	0 016	0.003	0.014	8	8	8	32	16	24	8	2	4	32	8	15
Basic	16	8	14	256	32	86	32	8	18	512	64	112	-	-	-
Phenolic	32	16	28	256	64	90	256	64	98	128	32	54	320	160	225
Neutral Fractions	32	16	25	64	16	32	128	4	19	64	8	26	128	32	64
1	16	8	11	-b	-	-	32	4	16	16	4	9	-	-	-
2	64	2	17	-	-	-	32	8	23	16	8	10	128	16	37
3	32	2	16	-	-	-	32	8	15	64	8	29	128	8	27
4	16	4	9	-	-	-	32	8	20	128	2	26	128	64	91
5	512	64	220	-	-	-	-	-	-	2560	160	840	10,000	5120	8000

a - Threshold tests were run by a panel of 4 to 7 observers and the geometric mean computed.

b - No odors on fractions because of partial decomposition during distillation.

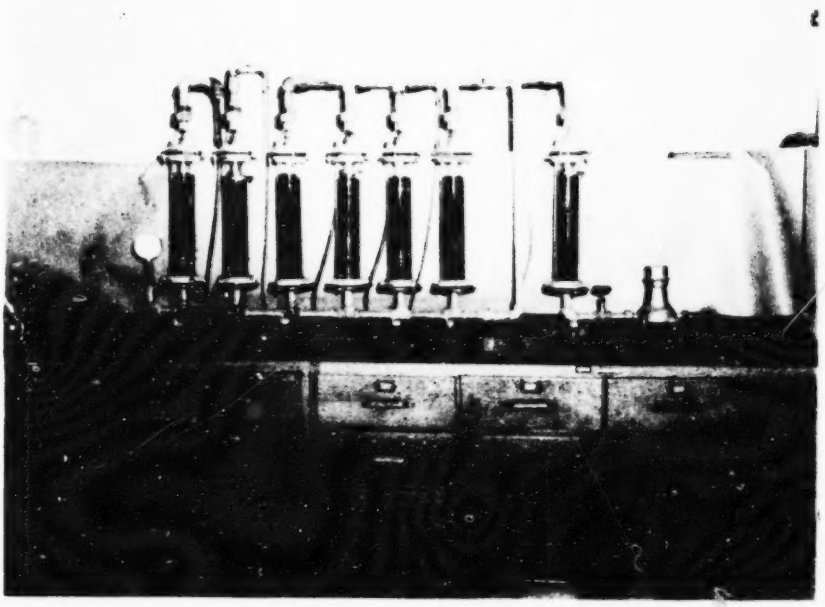

FIGURE 1

Carbon Filters for Tap Water Sampling

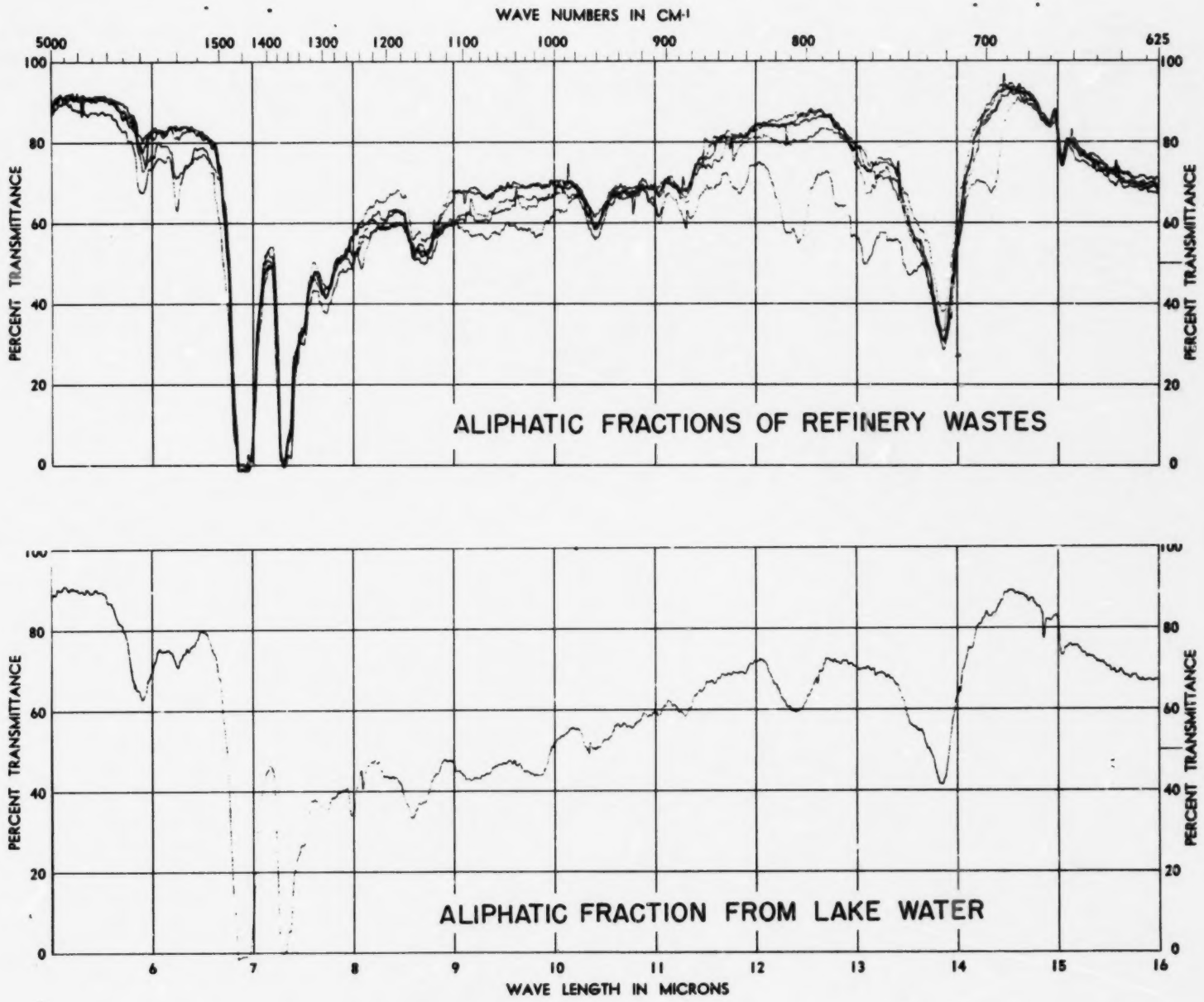

FIGURE 2. INFRARED SPECTRA OF ALIPHATIC MATERIALS

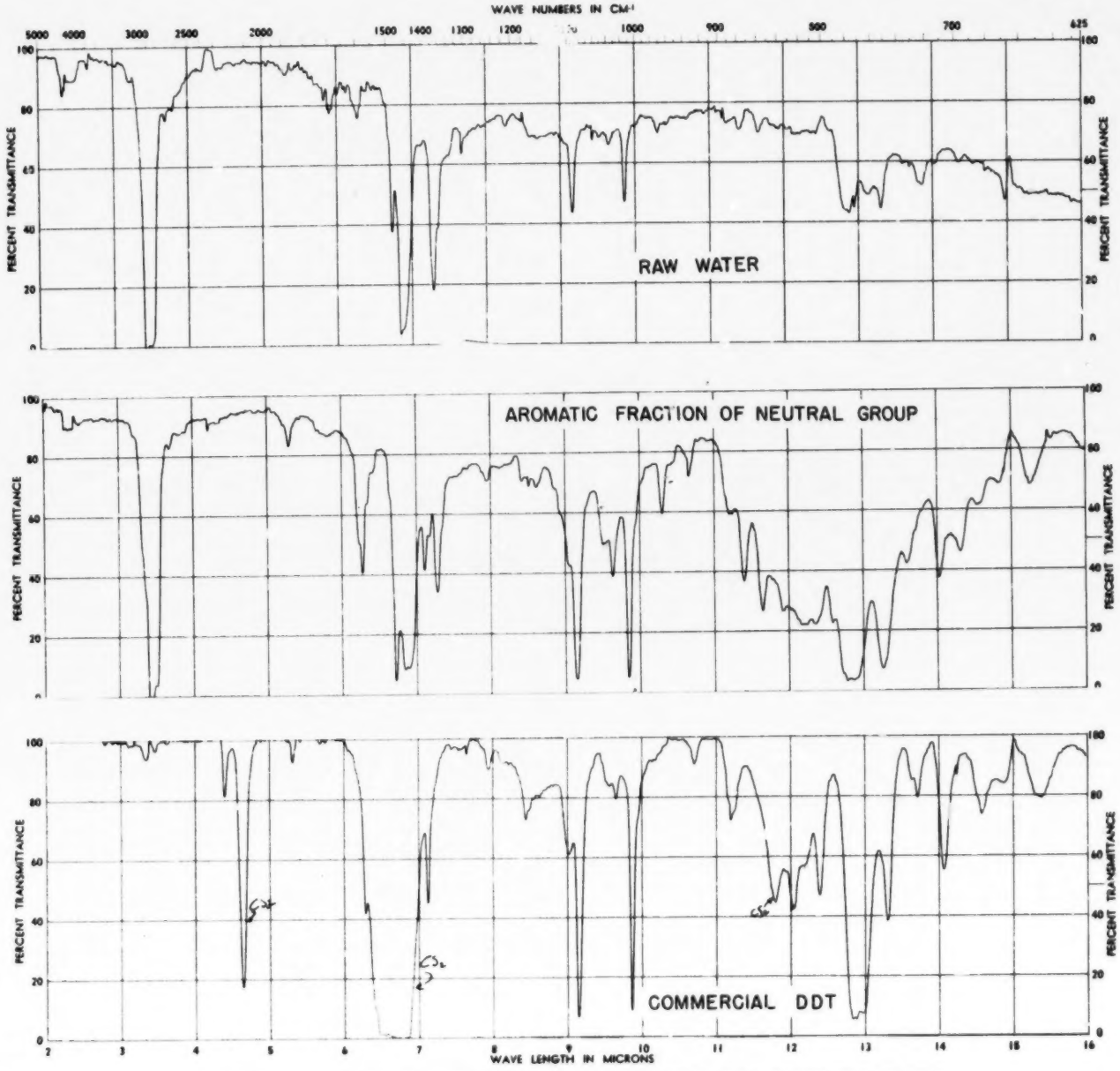
WAVE NUMBERS IN CM⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1000 900 800 700 625
PERCENT TRANSMITTANCE
RAW WATER
AROMATIC FRACTION OF NEUTRAL GROUP
COMMERCIAL DDT
WAVE LENGTH IN MICRONS
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16

FIGURE 3. INFRARED SPECTRA OF WATER EXTRACTS CONTAINING DDT

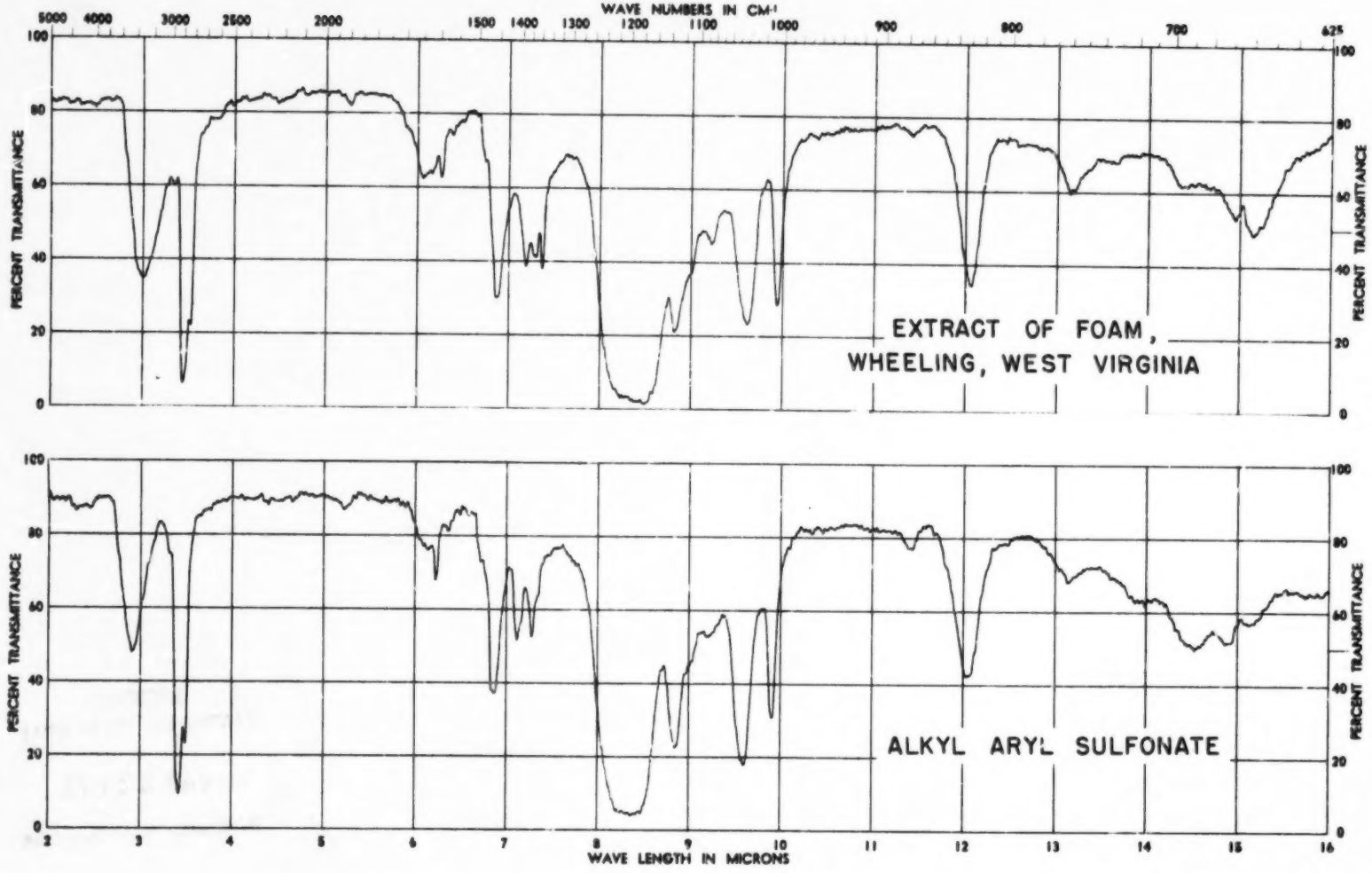
WAVE NUMBERS IN CM-1
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100 1000 900 800 700 625
PERCENT TRANSMITTANCE
EXTRACT OF FOAM,
WHEELING, WEST VIRGINIA
ALKYL ARYL SULFONATE
2 3 4 5 6 7 8 9 10 11 12 13 14 15 16
WAVE LENGTH IN MICRONS

FIGURE 4. INFRARED SPECTRA OF DETERGENT MATERIALS